The Ignition of Gases by Condenser Discharge Sparks.
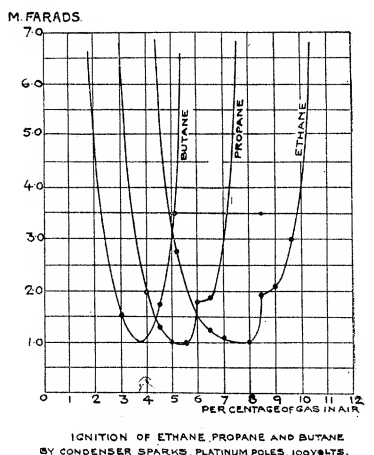
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1. It may be taken as an axiom of electrical ignition that the closer its conditions resemble those in the explosion wave front the more readily will it occur. These conditions are high temperature and pressure, and in the case of hydrocarbons combustion to carbon monoxide. They are also characteristic of condenser discharge sparks, for in the first place the surface of a platinum pole to which condenser discharge has been made becomes pitted to a remarkable extent, greater than when large currents are broken by separation of the poles. The sparks have therefore a high temperature. That they give rise to high gas pressure is clear from the intensity of the sound of a single spark discharge, and finally it will be shown that combustion to carbon monoxide rather than to carbon dioxide is peculiar in certain cases to ignition by capacity sparks. In addition to these the sparks are of very short duration, are oscillatory in character, and start with ionisation or breakdown of the gas between the poles. The belief that all visible sparks will ignite explosive mixtures no doubt arose from observations of the activity of condenser discharge in this respect, but while in certain cases, especially in the ignition of hydrogen, the least igniting sparks are very small, yet there is in every case a well marked limit to their igniting power, and as the percentage of gas limits of inflammability are approached they require to be large.

IGNITION OF ETHANE, PROPANE AND BUTANE
BY CONDENSER SPARKS, PLATINUM POLES, 100 VOLTS.

FIG. 1.

2. *The Paraffins—Ethane, Propane, and Butane.*—The gases used in the present work were from the same stocks as those used for break-spark ignition.* The results obtained from them are given in fig. 1. They have two interesting features; their minimum igniting current is the same in every case, in this resembling their ignition by continuous current break-

* "The Electrical Ignition of Gaseous Mixtures," W. M. Thornton, 'Roy. Soc. Proc.,' A, vol. 90, p. 272 (1914).

sparks, but they have the parabolic form characteristic of alternating current break-spark ignition. Ethane has, however, a minimum at 7·7 per cent., the point of combustion to carbon monoxide, the others, as before, midway between this and combustion to carbon dioxide. There is, however, on the higher side of the ethane and propane curves—the supply of butane gave out before this could be examined fully—a step or increase in difficulty of ignition corresponding to mixtures midway between four and five atoms of oxygen to one molecule of ethane, and between six and seven to one of propane. This point was thought to be some failure in the quality of the gas, but when it appeared in both, and to a still greater extent in methane, it was more fully examined. Condenser-spark ignition has therefore some of the features of both continuous and low frequency alternating current break-spark ignition, but it has a characteristic type of its own.

It may be remarked in passing that the energy per atom in unit volume of each of the three gases at the minimum of each curve is the same, in this resembling break-spark ignition.

3. *Methane.*—From the previous work it was expected that methane would have the same minimum as ethane, propane, and butane, but this was found to be not the case, and after several samples of pure methane, prepared at
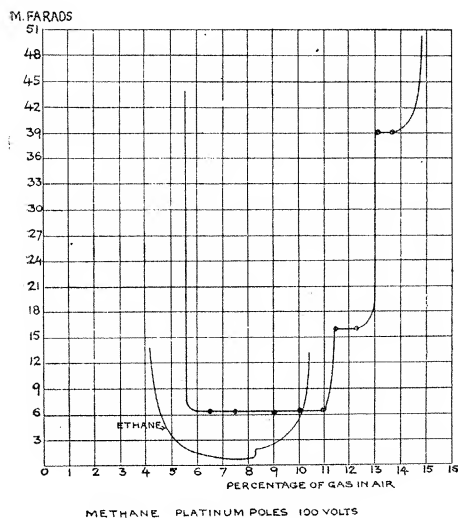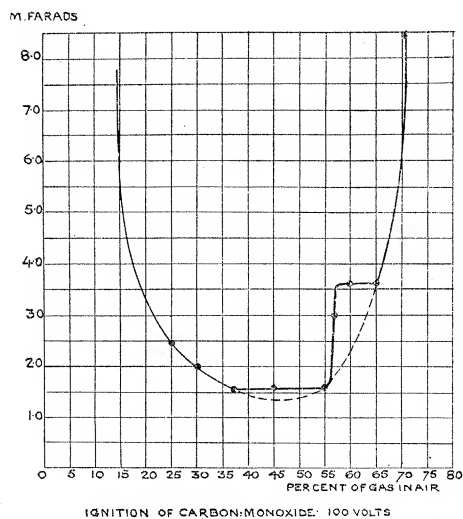

FIG. 2.

FIG. 3.

different times, had been very kindly sent to me by Dr. Wheeler for examination, the conclusion was reached that the mode of ignition of methane by condenser sparks was of an entirely new type, as shown in fig. 2. In the first place the energy required to obtain any ignition at all

was much greater than in the other paraffins; 6·5 microfarads had to be used at 100 volts as compared with 1 microfarad in the heavier gases. No ignition could be obtained below 6·25 per cent.; from this to 10·5 per cent. the energy of the least igniting spark was the same, but at 11·5 per cent. the necessary energy suddenly increased, so that nothing less than 16 microfarads would give an igniting spark. The mixture giving combustion to CO_2 had been passed through without change; combustion to CO is at 12 per cent. At 13 and 13·5 per cent. 40 microfarads had to be used, and above this no ignition could be obtained by condenser sparks with all the available capacity of 46 microfarads in use. The sparks were then of great brightness and pitted the poles freely. The stages may be more readily followed by a comparison of fig. 2 and Table I. The critical steps are at 11·5 and 13 per cent.

Table I.

Mixture.	Percentage of gas in air.
$2CH_4 + O_8$	9 ·36
$2CH_4 + O_7$	10 ·5
$2CH_4 + O_6$	12 ·0
$2CH_4 + O_5$	15 ·0

When the oxygen atoms are more in number than those of the combustible gas each stage appears to be symmetrical on either side of one of the critical percentages, when they are equal or less in number the step coincides with the critical percentage as in carbon monoxide and hydrogen. Numerical excess of oxygen therefore retards the rise of difficulty of ignition as much as possible, that is, half a stage.

4. *Carbon Monoxide.*—In order to see whether the ignition by steps occurred in other gases having a single carbon atom, carbon monoxide was examined (fig. 3). The figure is interesting on account of the well marked transition of stages. In the first from the lower limit to 37·5 per cent. the curve has the parabolic form. The mixture for complete combustion to CO_2 is at 29·2 per cent. and this is now passed through without notice, though with the break-sparks there is a change of type approaching 30 per cent.* At 37·5 per cent. a new stage is entered, from 37·5 to 56 per cent. the same igniting energy is required and the curve is horizontal. This clearly corresponds to an increase in difficulty of ignition, for the usual alternating current curve would fall below it. Above 65 per cent. the limit is rapidly approached,

* *Loc. cit.*, fig. 7.

and at 70 per cent. 28 microfarads are required for ignition. The meaning of the steps can be seen in Table II.

Table II.

Mixture.	Percentage of gas in air.
$2CO + O_2$	29·2
$3CO + O_2$	38·2
$4CO + O_2$	45·1
$6CO + O_2$	55·2
$9CO + O_2$	65·0
$12CO + O_2$	70·6

In this case there is an increase in difficulty of ignition as the combustible gas increases in multiples of 3.

5. *Hydrogen Sulphide.*—That these several steps are not peculiar to gases with single carbon atoms is shown by the behaviour of hydrogen sulphide (fig. 4). The gas was not specially purified and probably contained 1 per cent. of hydrogen; its limits of inflammability were observed to be at about 4·8 and 20 per cent. The steps occurred at 10 and 14 per cent., the mixtures being as in Table III.

Table III.

| Mixture.	Percentage of gas in air.
$H_2S + O_3$	17·1
$H_2S + O_4$	12·0
$H_2S + O_5$	7·6

Here the oxygen atoms are more in number than those of the combustible gas and these percentages are intermediate between the rising lines.

6. *Hydrogen.*—The ignition of hydrogen exhibits the stages very well, as shown in fig. 5. The observed steps are at 30, 45, 55, and 70 per cent., the upper limit being 72 per cent. As shown by Table IV the hydrogen atoms are more in number than the oxygen and the steps are at the critical mixtures.

Table IV.

Stage.	Mixture.	Percentage of gas in air.
1	$H_2 + O$	29·2
2	$2H_2 + O$	45·2
3	$3H_2 + O$	55·2
	$4H_2 + O$	62·2
	$5H_2 + O$	67·4
4	$6H_2 + O$	71·2

The coincidence between the mixtures with 1, 2, 3 and 6 hydrogen molecules to one oxygen atom and the observed steps are very close, and there cannot be any doubt that with certain gases of simple composition the play of forces upon an oxygen atom in the act of ignition can be observed in this way. The occurrence of ignition by steps has little or no relation to the other properties of the gas, and it may depend almost entirely on structure.
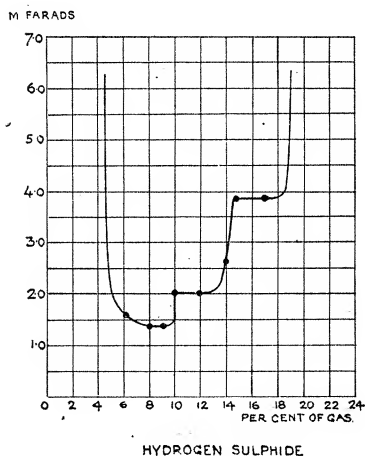
HYDROGEN SULPHIDE

Fig. 4.
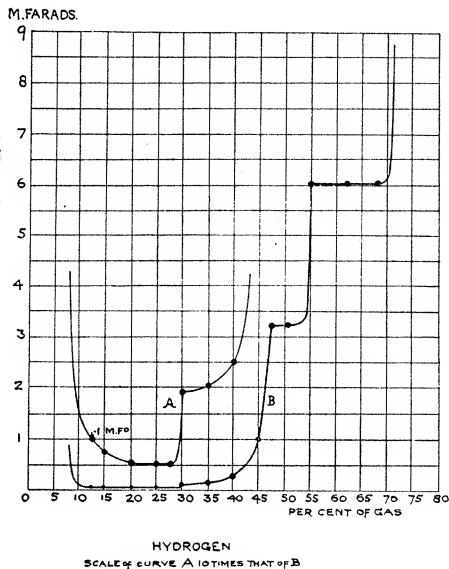
HYDROGEN
SCALE OF CURVE A 10 TIMES THAT OF B

Fig. 5.

7. *Cause of Stepped Ignition.*—The strongest argument that each rise in the curves is an increase in difficulty of ignition over that which would have normally been found in a purely thermal reaction is in the behaviour of methane. Here the first stage begins immediately after the lower limit. If there had been a gradual fall from this as in carbon monoxide or in the higher paraffins, it would by analogy with all previous results have reached the same level as ethane. The occurrence of a horizontal stage is not peculiar to condenser ignition, for it has been observed in the ignition of hydrogen and of carbon monoxide by break-sparks,* and in these cases also it indicated that more energy was required than if the rounded curve had been followed. In the present case the carbon monoxide curve presents the clearest evidence of the nature of the transition.

The cause of this increased resistance is probably that when an atom of combustible gas—or of oxygen in some cases—is surrounded by molecules with one or more of which it is eventually to combine, the difficulty of

* *Loc. cit.*, figs. 6 and 7.

choice of any single partner is increased by the simultaneous attraction of the others, and more energy must be given to the gas to set up a movement so violent that any pair is forced into " contact." In some cases, carbon monoxide for example, the difficulty of ignition only becomes acute in certain aggregates, thus the steps are at 3, 6, and 9 molecules of carbon monoxide to 1 of oxygen. In methane it is when there are 3 or 4 molecules of oxygen to 1 of methane. In hydrogen the critical ratios of hydrogen molecules to oxygen atoms are 1, 2, 3, and 6.

8. *Absolute Energy of Ignition.*—With carbon monoxide the energies of the two stages are 0·0082 and 0·018 joules, a ratio of 1 to 2·19, and there are twice as many molecules of CO in the second case. In methane the energies of the stages are 0·032, 0·8, 2 joules, in ratios $1:2\cdot5:6\cdot25$. In hydrogen sulphide the energies are 0·007, 0·01, 0·0195, in ratios $1:1\cdot43:2\cdot79$. In hydrogen the energies and ratios are as in Table V.

Table V.

Stage.	Energy of spark in joules.	Ratios.	
1	0 ·00025	1	
2	0 ·00095	3 ·8	3 ·8
3	0 ·0016	6 ·4	1 ·7
4	0 ·0030	12 ·0	1 ·87
		Mean	2 ·1

It would appear that the ratios of the energies in successive stages increase very approximately in a constant ratio 2, so that the difficulty of ignition is on an average doubled at each step. This is the more remarkable since the number of molecules in contact with a combining atom is not as a rule doubled. With more complex molecules the arrangement of atoms in the molecule will probably influence the relative ease of ignition.